

What is claimed is:

1. A flexible, thermoplastic, biaxially stretched, heat shrinkable film having at least one layer comprising a blend of at least three copolymers comprising:

25 to 85 weight percent of a first polymer having a melting point of from 55 to 95°C comprising at least one copolymer of ethylene and octene-1;

5 to 35 weight percent of a second polymer having a melting point of from 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of from 60 to 110°C comprising at least one unmodified or anhydride-modified copolymer of ethylene and a vinyl ester, acrylic acid, methacrylic acid or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers; and wherein said film has a shrinkage value at 90°C of at least 45% in at least one of the machine direction or transverse direction, and said film has a ram puncture force of at least 65 Newtons.

2. A polymer film, as defined in claim 1, wherein said first polymer has a melting point of from 80 to 85°C.

3. A polymer film, as defined in claim 1, wherein said first polymer is a bipolymer.

4. A polymer film, as defined in claim 1, wherein said first polymer is a terpolymer comprising: ethylene, hexene-1 and octene-1; or ethylene, butene-1 and octene.

5. A polymer film, as defined in claim 1, wherein said second polymer comprises a copolymer of ethylene and octene-1.

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~~6. A polymer film, as defined in claim 1, wherein said third polymer is selected from the group of ethylene vinyl acetate copolymer, ethylene methylacrylate copolymer, ethylene butylacrylate copolymer and ethylene ethylacrylate copolymer.~~

7. A film, as defined in claim 1, wherein said third polymer comprises a copolymer of ethylene and vinyl acetate.
8. A film, as defined in claim 1, further comprising a fourth polymer having a melting point of from 91 to 110°C.
9. A film, as defined in claim 1, having a haze value of less than 10%.
10. A film, as defined in claim 1, wherein said film has a shrinkage value at 80°C of at least 30% in at least one of the machine and transverse directions.
11. A film, as defined in claim 1, wherein said film has a shrinkage value at 80°C of at least 35% in at least one of the machine and transverse directions.
12. A film, as defined in claim 1, wherein said film has a shrinkage value at 80°C of at least 35% in both the machine and transverse directions.
- Sub B37** ~~13. A film, as defined in claim 1, wherein said film has a shrinkage value at 90°C of at least 45% in at least one of the machine and transverse directions.~~
14. A film, as defined in claim 1, wherein said film has a shrinkage value at 90°C of at least 45% in both the machine and transverse directions.
15. A film, as defined in claim 1, wherein said film has a total energy at maximum puncture force of at least 0.60 Joule.
16. A film, as defined in claim 1, wherein said film has a total energy at maximum puncture force of at least 0.80 Joule.
17. A film, as defined in claim 1, wherein said film has a total energy at maximum puncture force of at least 1.0 Joule.
18. A film, as defined in claim 1, wherein said film has a maximum ram puncture force of at least 100 Newtons.
19. A film, as defined in claim 1, wherein said film has a maximum ram puncture force of at least 110 Newtons.

20. A film, as defined in claim 1, wherein said film has a ram puncture stress of at least 140 MPa.

21. A film, as defined in claim 1, wherein said first polymer has a \bar{M}_w/\bar{M}_n of from 1.5 to 3.0.

22. A film, as defined in claim 1, wherein said first polymer has a \bar{M}_w/\bar{M}_n of from 2.2 to 2.7.

23. A film, as defined in claim 1, wherein said first polymer has a melt index of from 1.5 to 3.0 dg/min..

24. A film, as defined in claim 1, wherein said first polymer has a melt index of from 0.3 to 1.5 dg/min..

25. A film, as defined in claim 1, wherein said first polymer has a melt index less than 2.5 dg/min..

26. A film, as defined in claim 1, further comprising at least one additional other thermoplastic layer.

27. A film, as defined in claim 1, further comprising at least three additional thermoplastic layers.

Sub 28. A film, as defined in claim 1, wherein said blend containing layer has been irradiatively crosslinked.

29. A film, as defined in claim 1, wherein said layer is the innermost heat sealable layer of a tube formed of said film.

30. A film, as defined in claim 1, wherein said film is fabricated into bags.

31. A film, as defined in claim 26, wherein said additional layer comprises a gas barrier layer and said film has an oxygen transmission rate of less than 15 cc/100 in² for 24 hrs. at 1 atm. ^{at 230°C}

Sub 32. A film, as defined in claim 26, wherein said film is a tubular multilayer film formed by coextrusion or coating lamination and said blend comprises a heat sealing layer which is the innermost layer of said tube.

33. A film, as defined in claim 1, wherein said blend comprises at least 50 percent by weight

of said layer based on the total weight of the layer.

34. A film, as defined in claim 1, wherein said first polymer is present in an amount of from 25 to 45 weight percent, based upon the total weight of the first, second and third polymers.

35. A film, as defined in claim 1, wherein said first polymer is present in an amount of from 30 to 40 weight percent, based upon the total weight of the first, second and third polymers.

36. A film, as defined in claim 1, wherein said first polymer is present in an amount of from 45 to 85 weight percent, based upon the total weight of the first, second and third polymers.

37. A film, as defined in claim 1, wherein said first polymer is present in an amount of from 50 to 85 weight percent, based upon the total weight of the first, second and third polymers.

38. A film, as defined in claim 1, wherein at least one of said first, second, and third polymers comprises an interpolymer.

39. A film, as defined in claim 1, wherein at least one interpolymer comprises said first and second polymers.

Sub 40. A film, as defined in claim 27, wherein said film comprises:

a first heat sealing surface layer comprising a polymer selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

a second intermediate layer;

a third core layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

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~~a fourth surface layer;~~

~~wherein at least one of said second and said fourth layers comprise said three copolymer blend defined in claim 1, and said core layer is disposed between said second and said fourth layers.~~

41. A film, as defined in claim 40, wherein said film has a shrinkage value at 80 °C of at least 30% in at least one of the machine and transverse directions.

42. A film, as defined in claim 40 or 41, wherein said film has a tensile seal strength of at least 400 g/cm at 88°C.

43. A film, as defined in claim 40, wherein said film has a tensile seal strength of at least 600 g/cm at 88°C.

44. A film, as defined in claim 40 or 41, wherein said film has a hot water puncture resistance value of at least 40 seconds at 95°C.

45. A film, as defined in claim 40, wherein said film has a hot water puncture resistance value of at least 100 seconds at 95°C.

46. A film, as defined in claim 40 or 41, wherein said film has an average hot water seal strength of at least 200 seconds at 95°C.

47. A film, as defined in claim 40 or 41, wherein said film has an average hot water seal strength of at least 300 seconds at 95°C.

48. A film, as defined in claim 1 or 40, wherein said film has a ram puncture stress of at least 200 MPa..

49. A film, as defined in claim 40, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

50. A biaxially stretched, heat shrinkable film comprising a blend of: (i) an interpolymer comprising at least a copolymer of ethylene and octene-1 and having a first melting point of from 55 to 95°C and a second melting point of from 115 to 128°C, and (ii) a polymer having

a melting point of from 60 to 110°C comprising an unmodified or anhydride-modified copolymer of ethylene and a vinyl ester, acrylic acid, methacrylic acid, or alkyl acrylate; said film having a shrinkage value at 90°C of at least 45% in at least one of the machine and transverse directions.

51. A flexible, thermoplastic, biaxially stretched, heat shrinkable film having at least one layer comprising a blend of at least three copolymers comprising:

45 to 85 weight percent of a first polymer having a melting point of from 55 to 95°C comprising at least one copolymer of ethylene and octene-1;

5 to 35 weight percent of a second polymer having a melting point of from 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of from 60 to 110°C comprising at least one unmodified or anhydride-modified copolymer of ethylene and a vinyl ester, acrylic acid, methacrylic acid, or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers; and wherein said film has a total energy absorption of at least 0.70 Joule and a shrinkage value at 90°C of at least 50% in at least one of the machine and transverse directions.

52. A film, as defined in claim 51, wherein said blend comprises 50 to 85 weight % of said first polymer.

53. A film, as defined in claim 51, wherein said film has a maximum puncture force of at least 90 Newtons.

54. A film, as defined in claim 51, wherein said film has a shrinkage value at 80°C of at least 35% in at least one of the machine and transverse directions.

55. A film, as defined in claim 51, wherein said film has a shrinkage value at 80°C of at least 35% in both the machine and transverse directions.

56. A film, as defined in claim 51, wherein said film has a shrinkage value at 80°C of at least 50% in at least one of the machine and transverse directions.

57. A film, as defined in claim 51, wherein said film has a shrinkage value at 80°C of at least 50% in both the machine and the transverse directions.

58. A film, as defined in claim 51, wherein said film has a total energy absorption of at least 0.90 Joules.

59. A film, as defined in claim 51, wherein said film has a maximum stress of at least 200 MPa..

60. A film, as defined in claim 51 or 52, wherein at least one of said first, second, and third polymers comprises an interpolmer.

61. A film, as defined in claim 51, further comprising at least one additional thermoplastic layer.

62. A film, as defined in claim 51, further comprising at least four additional thermoplastic layers.

Sub 63. A film, as defined in claim 51 or 52, wherein said film comprises:

a first heat sealing surface layer comprising a polymer selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

a second intermediate polymeric layer;

a third core layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of vinylidene chloride with from 2 to 20 weight percent (based on

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and.
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~~said copolymer's weight) of vinyl chloride or methyl acrylate; and~~

~~a fourth surface polymeric layer;~~

~~wherein at least one of said second and said fourth layers comprise said three
copolymer blend defined in claim 54, and said core layer is disposed between said second and
said fourth layers.~~

64. A film, as defined in claim 63, wherein said film has a tensile seal strength of at least 400 g/cm at 88°C.

65. A film, as defined in claim 63, wherein said film has a hot water puncture resistance value of at least 40 seconds at 95°C.

66. A film, as defined in claim 63, wherein said film has a hot water puncture resistance value of at least 100 seconds at 95°C.

67. A film, as defined in claim 63, wherein said film has an average hot water seal strength of at least 200 seconds at 95°C.

68. A film, as defined in claim 63, wherein said film has an average hot water seal strength of at least 300 seconds at 95°C.

69. A film, as defined in claim 63, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

70. A biaxially stretched, heat shrinkable film comprising at least three layers, wherein said first layer comprises a blend of at least three polymers comprising: a first polymer having a melting point of from 55 to 95°C comprising a copolymer of ethylene and octene-1; a second polymer having a melting point of from 115 to 128°C comprising a copolymer of ethylene and at least one α -olefin; a third polymer having a melting point of from 60 to 110°C comprising a copolymer ethylene and a vinyl ester or alkyl acrylate; a third layer comprising at least 50 percent by weight of copolymer of ethylene with at least one alpha-olefin or at least one vinyl ester or blends thereof, and a second layer between said first and third layers; said

second layer comprising a vinylidene chloride copolymer, a nylon or a copolymer of ethylene with a vinyl alcohol; said film having a maximum ram puncture force of at least 65 Newtons, a total energy absorption of at least 0.50 Joule, and a shrinkage value at 90°C of at least 45% in at least one of the machine and transverse directions..

71. A film, as defined in claim 70, wherein said film has a shrinkage value at 90°C of at least 45% in both of the machine and transverse directions.

72. A film, as defined in claim 70, wherein said film has a shrinkage value at 80°C of at least 35% in at least one of the machine and transverse directions.

73. A film, as defined in claim 70, wherein said film has a maximum puncture force of at least 90 Newtons.

74. A film, as defined in claim 70, wherein said film has a total energy absorption of at least 0.9 Joule.

75. A film, as defined in claim 70, wherein at least one of said first, second, and third polymers comprises an interpolymer.

76. A film, as defined in claim 70, wherein at least one interpolymer comprises ^{both} said first and second polymers.

~~77. A polymer blend of at least three copolymers comprising:~~

~~25 to 85 weight percent of a first polymer having a melting point of from 55 to 95°C comprising at least one copolymer of ethylene and octene-1;~~

~~5 to 35 weight percent of a second polymer having a melting point of from 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and~~

~~10 to 50 weight percent of a third polymer having a melting point of from 60 to 110°C comprising at least one copolymer of ethylene and a vinyl ester or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and~~

third polymers.

78. A blend, as defined in claim 77, wherein said first polymer is present in an amount of from 25 to 45 weight percent, based upon the total weight of the first, second and third polymers.

79. A blend, as defined in claim 77, wherein said first polymer is present in an amount of from 30 to 40 weight percent, based upon the total weight of the first, second and third polymers.

80. A blend, as defined in claim 77, wherein said first polymer is present in an amount of from 45 to 85 weight percent, based upon the total weight of the first, second and third polymers.

81. A blend, as defined in claim 77, wherein said first polymer is present in an amount of from 50 to 85 weight percent, based upon the total weight of the first, second and third polymers.

82. A blend, as defined in claim 77, wherein at least one of said first, second, and third polymers comprises an interpolymer.

83. A blend, as defined in claim 77, wherein an interpolymer comprises ^{both} said first and second polymers.

84. A flexible film comprising at least one layer comprising the blend of claim 77.

~~85. A flexible film, as defined in claim 84, wherein said film comprises:~~

~~a heat sealing surface layer comprising a polymer selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a~~

melting point of at least 105°C and a density of at least 0.900 g/cm³:

an intermediate layer;

a core layer;

an outer protective surface layer;

wherein at least one of said intermediate and said outer protective layers comprise a polymer blend of at least three copolymers comprising:

25 to 85 weight percent of a first polymer having a melting point of from 55 to 95°C comprising at least one copolymer of ethylene and octene-1;

5 to 35 weight percent of a second polymer having a melting point of from 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of from 60 to 110°C comprising at least one unmodified or anhydride-modified copolymer of ethylene and a vinyl ester or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers.

and said core layer is disposed between said intermediate and said outer protective layers.

86. A process for making biaxially stretched, heat shrinkable film comprising:

extruding a melt plastified primary tube comprising 25 to 85 weight percent of a first polymer having a melting point of from 55 to 95°C comprising at least one copolymer of ethylene and octene-1;

5 to 35 weight percent of a second polymer having a melting point of from 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of from 60 to 110°C comprising at least one copolymer of ethylene and a vinyl ester or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight

percent, said weight percentage being based upon the total weight of said first, second and third polymers;

cooling said primary tube;

reheating said cooled tube to a draw point temperature of from 68 to 88°C;

biaxially stretching said tube to a circumference of at least 2½ times the circumference of said primary tube, and cooling said biaxially stretched tube to form a biaxially stretched, heat shrinkable film.

87. A process, as defined in claim 86, wherein said draw point temperature is of from 65 to 79°C.

88. A process, as defined in claim 86, wherein said resultant film has a maximum ram puncture force of at least 65 Newtons, a total energy absorption of at least 0.50 Joule, and a shrinkage value at 90°C of at least 45% in at least one of the machine and transverse directions.

89. A process, as defined in claim 86, wherein said blend comprises at least 50% of said first polymer.

90. A process, as defined in claim 86, wherein said resultant film has a maximum ram puncture force of at least 90 Newtons, a total energy absorption of at least 0.90 Joule, and a shrinkage value at 90°C of at least 50% in both of the machine and transverse directions.

91. A process, as defined in claim 86, wherein a multilayer primary tube is made by coextrusion or coating lamination and said resultant biaxially stretched film comprises:

a heat sealing surface layer comprising a polymer selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of

propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³:

an intermediate layer;

a core layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of EVOH; or vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

an outer protective surface layer;

wherein at least one of said intermediate and said outer protective layers comprise said blend defined in claim 77, and said core layer is disposed between said intermediate and said outer protective layers, and said film has a maximum ram puncture force of at least 100 Newtons, a hot water puncture resistance of at least 100 seconds at 95°C and a hot water seal strength of at least 200 seconds at 95°C.

92. A process, as defined in claim 86, wherein at least one of said first and second polymers comprise: a terpolymer of ethylene, butene-1 and octene-1; or ethylene, hexene-1 and octene-

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93. A biaxially stretched, heat shrinkable, multilayer film useful for food processing and packaging having at least four layers comprising:

a first heat sealing surface layer comprising a polymer or blend of polymers selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. % and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

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a second polymeric layer comprising a blend of (a) from 25 to 85% of a first polymer having a melting point of 55 to 95°C comprising a copolymer of ethylene and octene-1; (b) from 5 to 35% of a second polymer having a melting point of 115°C to 128°C comprising a copolymer of ethylene and at least one C₄-C₈ α-olefin; and (c) from 10 to 50% of a third polymer having a vinyl ester melting point of 60 to 110°C comprising a copolymer of ethylene with a vinyl ester (preferably 4 to 18% by weight of said copolymer), acrylic acid, methacrylic acid, or alkyl acrylate (preferably 4 to 30% alkyl acrylate by weight of said copolymer), wherein said first and second copolymers have a combined weight percentage of at least 50 weight percent, said weight percent being based upon the total weight of said first, second and third polymers;

a third layer comprising at least 80% by weight (based on said third layer's weight) of EVOH or at least one copolymer of vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

a fourth polymeric layer comprising (a) from 10 to 85% of a first copolymer of ethylene and at least one C₃-C₈ α-olefin, said first copolymer having a melting point of 55 to 98°C, (b) from 5 to 60% of a second copolymer of ethylene and at least one C₄-C₈ α-olefin, said second copolymer having a melting point of 115°C to 128°C, and (c) from 0 to 50% of a third copolymer having a melting point of 60 to 110°C of ethylene with a vinyl ester (preferably 4 to 18%), acrylic acid (preferably 4 to 30%), methacrylic acid, or alkyl acrylate, wherein said first and second copolymers have a combined weight percentage of at least 50 weight percent, said weight percent being based upon the total weight of said layer; and

wherein said film has a shrinkage value at 90°C of at least 40% in at least one of the machine and transverse directions, and said film has a tensile seal strength of at least 400 g/cm at 88°C.

94. A film, as defined in claim 93, wherein said film has a maximum ram puncture force of

at least 70 Newtons.

95. A film, as defined in claim 93, wherein said film has a maximum ram puncture force of at least 110 Newtons.

96. A film, as defined in claim 93, wherein said film has a hot water puncture resistance of at least 25 seconds at 95°C.

97. A film, as defined in claim 93, wherein said film has a hot water puncture resistance of at least 40 seconds at 95°C.

98. A film, as defined in claim 93, wherein said film has a hot water puncture resistance of at least 100 seconds at 95°C..

99. A film, as defined in claim 93, wherein said film has a hot water seal strength of at least 200 seconds at 95°C.

100. A film, as defined in claim 93, wherein said film has a hot water seal strength of at least 300 seconds at 95°C.

101. A film, as defined in claim 93, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

102. A film, as defined in claim 93, wherein said film has a thickness less than 175 microns.

103. A film, as defined in claim 93, wherein said film has a haze value of less than 10% and a gloss at 45° of at least 70 Hunter units.

104. A film, as defined in claim 93, wherein said film has an oxygen transmission rate of less than 45 cm³/m² for 24 hrs. at 1 atm. at 23°C.

105. A film, as defined in claim 93, wherein said first copolymer of at least one of said second and fourth layers has a density less than 0.900 g/cm³.

106. A film, as defined in claim 93, wherein said first copolymer of both said second and fourth layers has a density less than 0.900 g/cm³.

~~107. A film, as defined in claim 93, wherein said third copolymer of both said second and~~

fourth layers comprises 4 to 18 % (by weight of said copolymer) of a vinyl ester or 4 to 30% of an alkyl acrylate.

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108. A film, as defined in claim 93, wherein in said fourth polymeric layer comprises a blend of: (a) from 25 to 85% of a first polymer having a melting point of 55 to 95°C comprising a copolymer of ethylene and octene-1; (b) from 5 to 35% of a second polymer having a melting point of 115°C to 128°C comprising a copolymer of ethylene and at least one C₄-C₈ α-olefin; and (c) from 10 to 50% of a third polymer having a melting point of 60 to 110°C comprising a copolymer of ethylene with a vinyl ester, acrylic acid, methacrylic acid, or alkyl acrylate, wherein said first and second copolymers have a combined weight percentage of at least 50 weight percent, said weight percent being based upon the total weight of said first, second and third polymers.

109. A film, as defined in claim 93, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

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110. A film, as defined in claim 93, wherein said copolymer of ethylene and octene-1 is present in an amount of 50 to 85% of said layer.

111. A film, as defined in claim 93, wherein said copolymer of ethylene and octene-1 is present in an amount of 25 to 50%.

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